Synthesis and structural characterization of LiI, ZnII, CdII, and HgII complexes containing a fluorinated -diketiminate ligand

Liu, Jingjing ; Vieille-Petit, L ; Linden, Anthony ; Luan, X ; Dorta, R

Abstract: The reaction of a fluorinated -aminoimine compound ArN]C(Me)CH]C(Me)NHAr (1) (Ar = 2,6-F2C6H3) with n-BuLi in coordinating solvents (Et2O and THF) leads to the solvated complexes [HC(CMeNAr)2]Li(Et2O) (2) and [HC(CMeNAr)2]Li(THF) (3), respectively. They exist as momonuclear complexes featuring lithium atoms in a distorted trigonal planar environment. The same reaction, which was then carried out in a non-coordinated solvent (pentane), provided complex [HC(CMeNAr)2]2Li2 (4). It crystallized as a dinuclear complex in the solid state, featuring lithium atoms in a pseudo-tetrahedral coordination environment. Notably, one fluorine atom of each ligand was involved to stabilize the lithium center. Taking complex 2 as the precursor, a series of group 12 metal complexes were prepared via the reaction with MX2 (M = Zn, Cd, Hg; X = Br, I). The diketiminate zinc complexes [HC(CMeNAr)2]Zn(-I)2Li(Et2O)2 (5) and [HC(CMeNAr)2]Zn(-Br)2Li(Et2O)2 (6) were successfully synthesized and characterized by single crystal X-ray diffraction analysis. When 2 reacted with CdI2, the expected double iodide bridging product [HC(CMeNAr)2]Cd(-I)2Li(Et2O)2 (7a) was only generated in a small amount, with the single iodide bridging complex HC(CMeNAr)2Cd(I)(-I)Li(Et2O)3 (7b) as the major product. These results were unambiguously confirmed by NMR spectroscopy and X-ray crystallography. Next, a mercury complex [HC(CMeNAr)2]Hg(-I)2Li(Et2O) (8) was prepared by using HgI2 as the metal source. Additionally, [HC(CMeNAr)2]ZnEt (9) was also obtained by mixing ligand 1 with Et2Zn.

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Synthesis and structural characterization of Li^{I}, Zn^{II}, Cd^{II}, and Hg^{II} complexes containing a fluorinated β-diketiminate ligand

Jingjing Liu[a,b]*, Ludovic Vieille-Petit[c], Anthony Linden[c], Xinjun Luan[a]*, Reto Dorta[c]

[a] *Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of the Ministry of Education, College of Chemistry & Materials Science, Northwest University, Xi'an, Shaanxi 710069, P. R. China*

[b] *CEA, IRAMIS, SPAM, LFP, 91191 Gif/Yvette, France*

[c] *Institute of Organic Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057, Zurich, Switzerland*

* Corresponding author.

E-mail address: jj.liu209@gmail.com (JL) and xluan@nwu.edu.cn (XL)

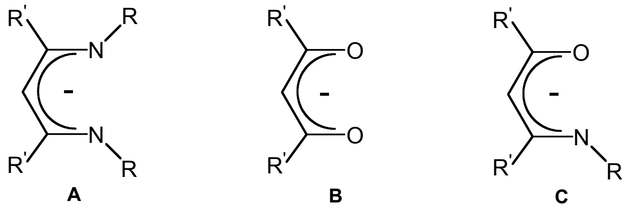
ABSTRACT

The reaction of a fluorinated β-aminoimine compound ArN=C(Me)CH=C(Me)NHAr (**1**) (Ar = 2,6-$F_2C_6H_3$) with *n*-BuLi in coordinating solvents (Et_2O and THF) led to the solvated complexes $[HC(CMeNAr)_2]Li(Et_2O)$ (**2**) and $[HC(CMeNAr)_2]Li(THF)$ (**3**), respectively. They exist as monomers featuring lithium atoms in a distorted trigonal planar environment. The same reaction, which was then carried out in a non-coordinated solvent (pentane), provided complex $[HC(CMeNAr)_2]_2Li_2$ (**4**). It crystallized as a dimer in the solid state, featuring lithium atoms in a pseudo-tetrahedral coordination environment. Notably, one fluorine atom of each ligand was involved to stabilize the lithium center. Taking complex **2** as the precursor, a series of group 12 metal complexes were prepared via the reaction with MX_2 (M = Zn, Cd, Hg; X = Br, I). The diketiminate zinc complexes $[HC(CMeNAr)_2]Zn(\mu\text{-}I)_2Li(Et_2O)_2$ (**5**) and $[HC(CMeNAr)_2]Zn(\mu\text{-}Br)_2Li(Et_2O)_2$ (**6**) were successfully synthesized and characterized by single-crystal X-ray diffraction analysis. When it reacted with CdI_2, the expected double iodide bridging product $[HC(CMeNAr)_2]Cd(\mu\text{-}I)_2Li(Et_2O)_2$ (**7a**) was only generated at a small amount, with the single iodide bridging complex $\{HC(CMeNAr)_2\}Cd(I)(\mu\text{-}I)Li(Et_2O)_3$ (**7b**) as the major product. These results were unambiguously confirmed by NMR spectroscopy and X-ray studies. Next, a mercury complex $[HC(CMeNAr)_2]Hg(\mu\text{-}I)_2Li(Et_2O)$ (**8**) was prepared

by using HgI_2 as the metal source. Additionally, $[HC(CMeNAr)_2]ZnEt$ (**9**) was also obtained by mixing ligand **1** with Et_2Zn.

1. Introduction

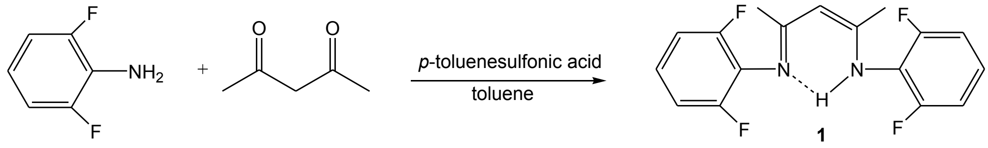
The sterically encumbered *β*-diketiminates (**A**) are one of the most useful motifs for monoanionic, nitrogen-based bidentate ligands in organometallic chemistry[1]. Although the *β*-diketonato (**B**)[2] and *β*-enaminoketonato (**C**)[3-4] ligands are the traditionally popular chelating systems, the isoelectronic *β*-diketiminato ligands have recently gained dramatically increasing attention, due to the ease variation of R groups on the nitrogen, which may be hydrogen, alkyl, aryl, or silyl groups[5-6].



In the past decade, the use of *β*-diketiminates as supporting ligands was extensively studied, and a wide range of main group element[7-11], transition metal[12-16] and lanthanide complexes[17-18] containing this type of ligands have been reported. Importantly, a good number of these metal complexes have proven to serve as effective catalysts for olefin polymerization[19], silane dehydropolymerization[20], olefin hydrosilylation[21], lactide polymerization[22], Suzuki coupling[23], hydroamination[24], and other transformations. Much of the related work has focused on the *β*-diketiminate derivatives in which the nitrogen atoms being linked with bulky substituents such as 2,6-diisopropylphenyl groups[25-27]. Encouraged by the very rich chemistry already displayed by this valuable ligand, it is attractive to synthesize its analogues and explore the potential applications. Consequently, several research groups have investigated a variety of ligands by varying both the steric and electronic factors based on the *β*-diketiminate framework[28-34]. In this context, we describe the synthesis and structural analysis of a series of new lithium, zinc, cadmium, and mercury complexes derived from a fluorinated *β*-diketiminate ligand.

2. Results and discussion

By reaction of 2,4-pentanedione with two equivalents of 2,6-difluoroaniline in the presence of *p*-toluenesulfonic acid in refluxing toluene, the fluorinated *β*-diketimine derivative **1** was prepared in good yield (Scheme 1)[35].



Scheme 1. Synthesis of fluorinated β-diketimine **1**

After recrystallization in cold diethyl ether, large crystals were obtained and analyzed by X-ray structure analysis, confirming the molecular structure of **1** (Figure 1).

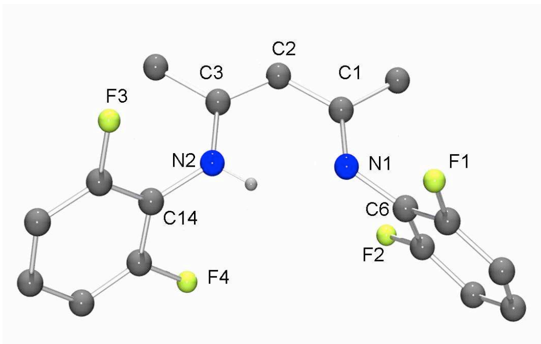
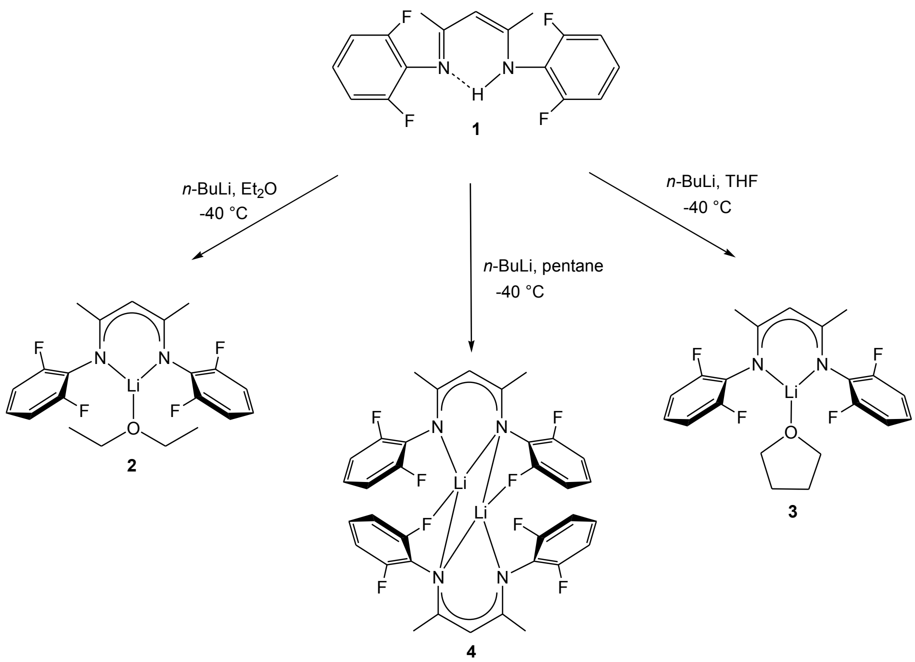


Figure 1. Molecular structure of **1**. H atoms, excepted for N-H are omitted for clarity.

Treatment of **1** with *n*-BuLi in Et_2O, THF or pentane resulted in the products **2**, **3** or **4** in good yields (Scheme 2).



Scheme 2. Treatment of **1** with *n*-BuLi in different solvents

The reaction of **1** with *n*-Buli in coordinating solvents (Et_2O and THF) gave rise to the solvated complexes $[HC(CMeNAr)_2]Li(Et_2O)$ (**2**) and $[HC(CMeNAr)_2]Li(THF)$ (**3**), respectively. Both complexes were fully characterized by ^{1}H, ^{13}C and $^{19}F\{^{1}H\}$ NMR spectroscopy. Complex **2** was further characterized by X-ray structure analysis, after crystallization in a cold Et_2O solution. Its molecular structure is shown in Figure 2. Complex **2** crystallized as a monomer featuring lithium center in a distorted trigonal planar environment, with a N-Li-N angle value of 97.6(2)º and O-Li-N angle values of 124.9(2)º and 136.6(2)º. The Li-N and Li-O bond lengths [1.930(4) and 1.892(4) Å, respectively] are within the range of those previously observed for three coordinate lithium bound to amide and ether ligands.[36] The $^{19}F\{^1H\}$ NMR spectra of **2** and **3** show a sharp signal at -124.69 and -123.75 ppm, respectively. In the case of **3**, crystals suitable for X-ray analysis couldn't be obtained, the presence of the THF molecule coordinated on the lithium center was concluded by NMR spectroscopy, the ^1H NMR spectrum showing two corresponding signals centerd at 3.35 and 1.21 ppm, with the right integration.

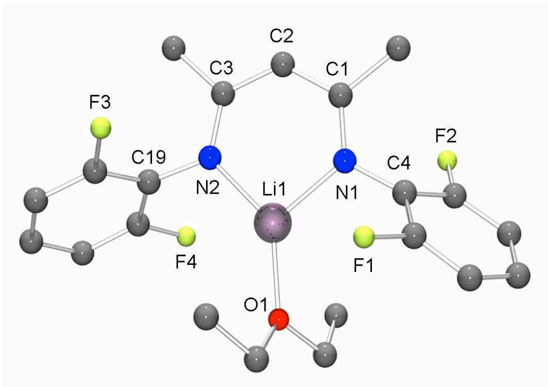


Figure 2. Molecular structure of **2**. H atoms are omitted for clarity.

When the same reaction was carried out in a non-coordinating solvent (pentane), complex $[HC(CMeNAr)_2]_2Li_2$ (**4**) was obtained. Crystals of **4** were grown in cold hexane and the X-ray structure analysis was performed. Complex **4** crystallized as a dimer, featuring lithium atoms in a pseudo-tetrahedral environment, both lithium centers being chelated by one bidentate *β*-aminoiminate ligand [Li-N distances: 1.927(3) and 1.995(3) Å] and, very interestingly, stabilized by coordination of one nitrogen atom [Li-N distance: 2.156(3) Å] as well as one of the fluorine atoms [Li-F distance: 2.005(3) Å] from a neighbour ligand, as shown in Figure 3. Power et al. also reported a non-fluorinated *β*-diketiminate-lithium complex generated in a non-coordinating solvent (hexane), in which the lithium centers were stabilized by the ligand and its aromatic rings.[36] In sharp contrast to this know example, the lithium centers of complex **4** are stabilized by the *β*-diketiminate ligand and the fluorine substituents.

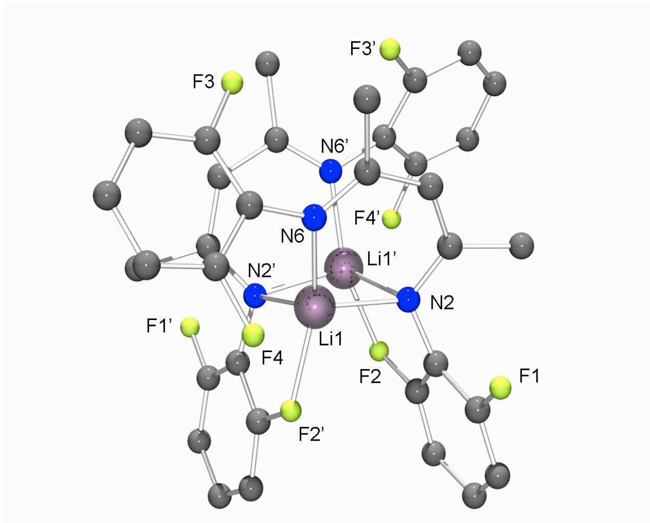
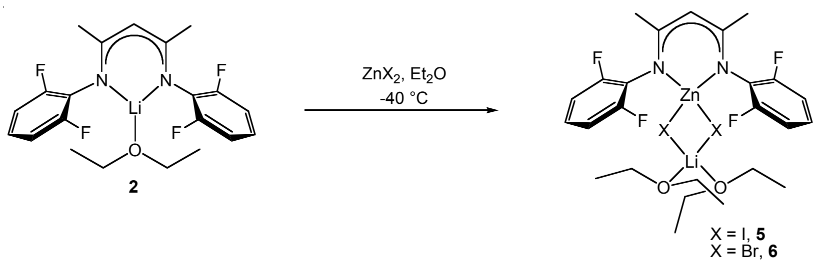


Figure 3. Molecular structure of **4**. H atoms are omitted for clarity.

In order to evaluate the possibility of using this new fluorinated ligand to bind transition metals, we mixed different metal precursors with the ligand transferring reagent **2**. Specifically, we have focused on the synthesis of monomeric complexes [HC(CMeNAr)$_2$]MX (M= Zn, Cd, Hg; Ar = 2,6-$F_2C_6H_3$) by considering the sterically demanding and chelating properties of **1**. Furthermore, based on the results observed in the molecular structure of compound **4**, we presumed that fluorine atoms could facilitate to stabilize the metal centers.

By reaction of starting material **2** with ZnX_2 (X = I, Br) in Et_2O, two complexes [HC(CMeNAr)$_2$]Zn(μ-I)$_2$Li(Et_2O)$_2$ (**5**) and [HC(CMeNAr)$_2$]Zn(μ-Br)$_2$Li(Et_2O)$_2$ (**6**) were obtained quite smoothly as single reaction products in good yields (Scheme 3). Molecular structures of **5** and **6** are shown Figure 4 and 5, respectively. Both complexes consist of halogen-bridged units, the lithium centers being stabilized by coordination of two molecules of Et_2O, as proved by X-ray structure analysis. Moreover, the structure of **5** in solution is consistent with its solid state structure, which is confirmed by ^{1}H NMR spectrum. It is worth of mentioning that complexes **5** and **6** are moisture sensitive, giving back to **1** as the primary hydrolysis product in the presence of water.



Scheme 3. Preparation of [HC(CMeNAr)$_2$]Zn(μ-I)$_2$Li(Et_2O)$_2$ (**5**) and [HC(CMeNAr)$_2$]Zn(μ-Br)$_2$Li(Et_2O)$_2$ (**6**)

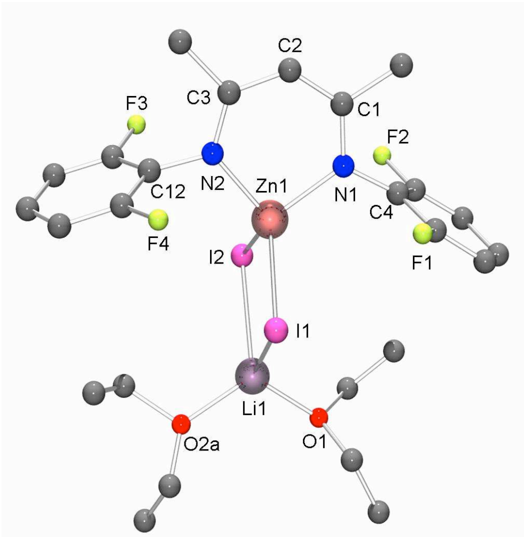


Figure 4. Molecular structure of **5**. H atoms are omitted for clarity.

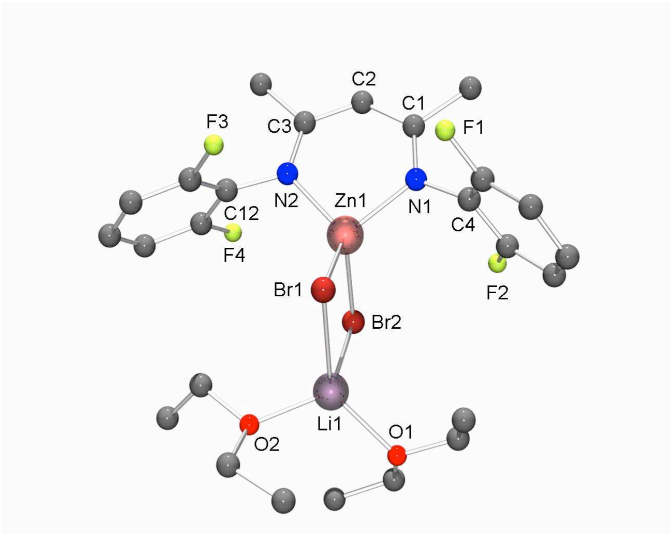
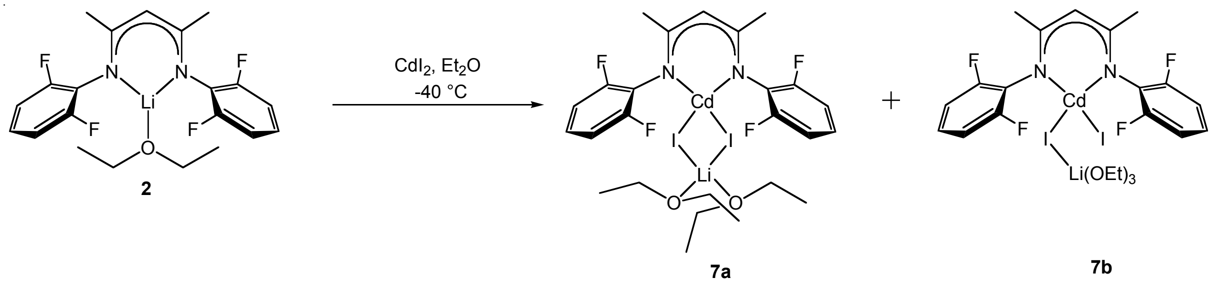


Figure 5. Molecular structure of **6**. H atoms are omitted for clarity.

In both cases, the central structural element is a [HC(CMeNAr)$_2$](μ-X)$_2$Li unit. The diketiminate ligand acts as a chelating ligand through its two N atoms, forming a six-membered ring with the zinc atom. The Zinc center and the lithium cation are bridged by the two iodine or bromine atoms, respectively. The N-Zn-N angle is 96.9(2)º in the case of **5** and 96.7(2)º in the case of **6**, and the X-Zn-X is 102.69(2)º for **5** and 101.26(2)º for **6**. The tetrahedral coordination geometry of the metal is distorted due to the strain imposed by the six-membered ring of the chelate, and the four-membered ring of the bridging halides. These structures are comparable to that of a zinc complex derived from the ligand bearing 2,6-diisopropylphenyl substituents[7].

Under the same reaction conditions as the above examples, mixing **2** with CdI_2, the expected double iodide bridging compound [HC(CMeNAr)$_2$]Cd(μ-I)$_2$Li(Et$_2$O)$_2$ (**7a**) was just obtained as a minor product (18%), while the major product is [HC(CMeNAr)$_2$]Cd(I)(μ-I)Li(Et$_2$O)$_3$ (**7b**) containing a single iodide bridge (82%) (Scheme 4). Clearly, the reactivity of this β-diketiminate ligand was influenced by its fluorine substituents, since the known non-fluorinated β-diketiminate ligand only gave one kind of product which is similar to **7a**.[7]



Scheme 4. Reaction of **2** with CdI_2

The molecular structures of **7a** and **7b** were revealed by single crystal X-ray diffraction studies (Figures 6 and 7). Crystals suitable for X-ray structure analysis were grown by slow evaporation of a saturated Et$_2$O solution of the mixture at room temperature. The molecular structure of **7a** is an analogue of **5** and **6**, while **7b** possesses only one iodide bridging ligand, with the second iodine atom being terminally attached on the cadmium center. In the structure of **7a**, the average bond distance between cadmium and iodide centers is 2.760(2) Å, which is shorter than Cd2-I3 bond [2.787(2) Å] and longer than Cd2-I4 bond [2.724(2) Å] in **7b**; the average bond distance between lithium and iodide centers is 2.872(2) Å, which is clearly shorter than Li2-I3 bond [2.950(2) Å] in **7b**. Additionally, the fact that lithium center is stabilized by the coordination of three Et$_2$O molecules was illustrated by ^{1}H NMR spectroscopy as well.

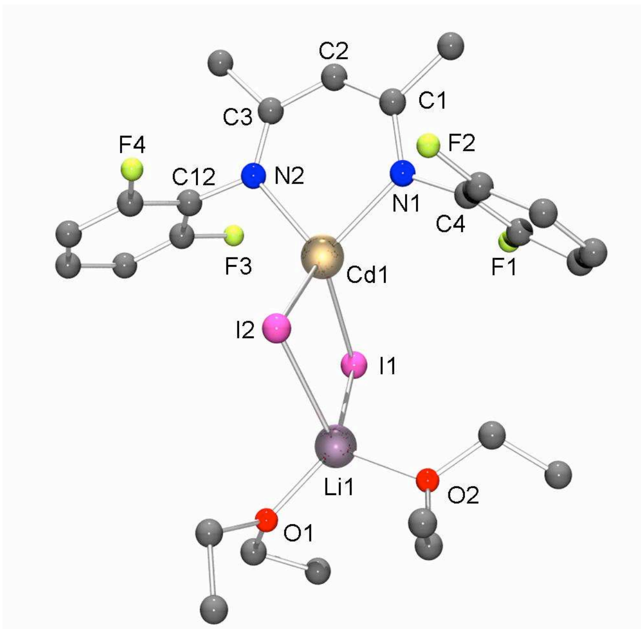


Figure 6. Molecular structure of **7a**. H atoms are omitted for clarity.

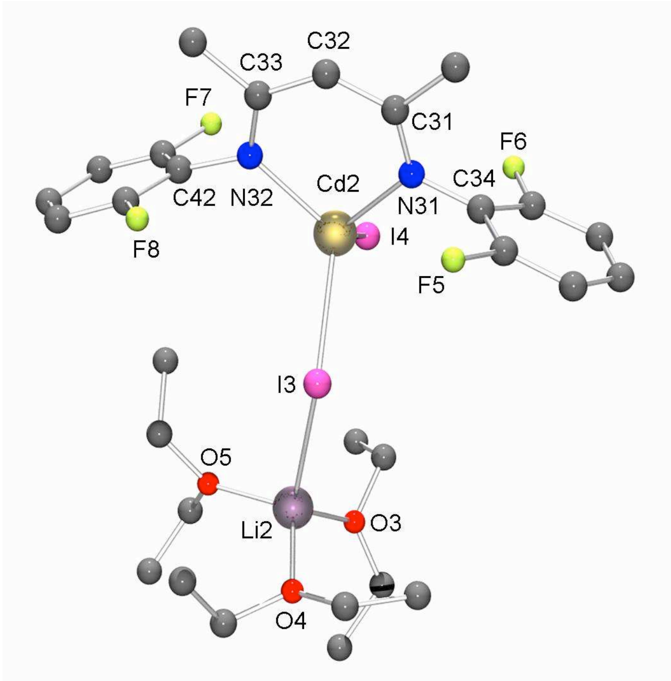
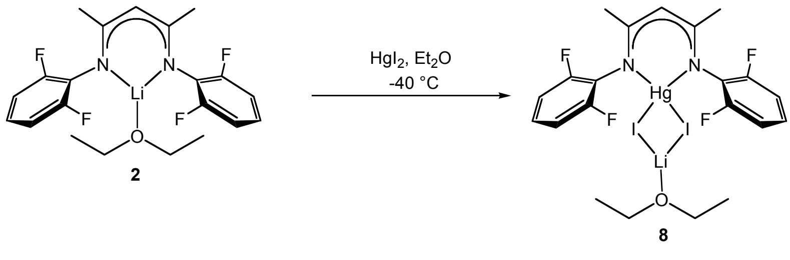


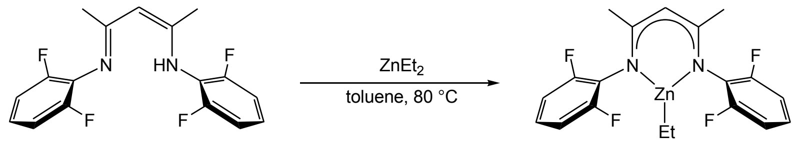
Figure 7. Molecular structure of **7b**. H atoms are omitted for clarity

In the case of reacting **2** with HgI_2, a uncommon mercury complex $[HC(CMeNAr)_2]Hg(\mu\text{-}I)_2Li(Et_2O)$ (**8**) was also synthesized (Scheme 5). To our knowledge, this is the first example of Hg/Li bimetallic complex derived from a *β*-diketiminate ligand. After carefully analyzing its ^1H NMR spectrum, we found it had the similar bimetallic regime as their zinc and cadmium analogues, but only one Et_2O molecule was adequate to stabilize the active lithium center.



Scheme 5. Synthesis of $[HC(CMeNAr)_2]Hg(\mu\text{-}I)_2Li(Et_2O)$ (**8**)

This fluorinated *β*-diketiminate ligand **1** can not only be employed to prepare four-coordinated zinc, cadmium, and mercury complexes **5-8**, but also can be used to synthesize three-coordinated zinc complex **9** $[HC(CMeNAr)_2]ZnEt$ (Scheme 6). Following a convenient synthetic route known in the literature[37], complex **9** was prepared in quantitative yield via the reaction of ligand **1** with Et_2Zn. Its structure was successfully elucidated by NMR spectroscopy.



Scheme 6. Synthesis of $[HC(CMeNAr)_2]ZnEt$ (**9**)

3. Conclusions

In conclusion, we have studied the coordination behaviour of a fluorinated *β*-diketiminate ligand **1** with lithium, zinc, cadmium, and mercury precursors. Unlike the mostly used *β*-diketiminate ligand $[HC(CMeNAr)_2]$ (Ar = 2,6-diisopropylphenyl), ligand **1** allowed the formation of a novel lithium complex **4** in which the interaction between a fluorine atom of **1** and the lithium center was observed; ligand **1** enabled the synthesis of a series of bimetallic M-Li (M = Zn, Cd, Hg) complexes **5**-**8**, with the lithium center being stabilized by two, three and one molecule of Et_2O in its zinc, cadmium and mercury complex, respectively; ligand **1** could also be utilized to obtain a low coordinated zinc complex **9**.

4. Experimental

4.1. General information

All reactions were carried out under an inert atmosphere of nitrogen using Schlenk or glovebox (Innovative Technology) techniques. All reagents were used as received unless otherwise noted. Solvents were purchased in the best quality available, purged with argon and collected after passage through alumina columns in a solvent purification system (Innovative Technology). Deuterated NMR solvents were purchased from Cambridge Isotope Laboratories Inc. and dried over activated molecular sieves of appropriate size. NMR spectra were recorded using a Bruker ARX-300 spectrometer. Mass spectra were recorded by the analytical service of the University of Zurich.

*4.2 Synthesis of ligand (**1**)*

A mixture of 2,6-difluoroaniline (13.5 mL, 0.125 mol), 2,4-pentanedione (6.2 mL, 0.06 mol), and *p*-toluenesulfonic acid (10.65 g, 0.06 mol) was refluxed in toluene (175 mL) for 24 h. The resulted precipitate was filtered and then treated with a mixture of diethyl ether (200 mL), water (100 mL), and Na_2CO_3 (26 g). After being vigorously stirred for 30 minutes, the ether layer was decanted, separated and the aqueous phase extracted with 75 mL of ether. The organic phases were combined and dried over $MgSO_4$. After filtration and concentration under vacuum, the solution was placed in the fridge (- 40 ºC), to give pale-yellow crystals of **1**, suitable for X-ray structure analysis, which were filtered and dried *in vacuo*. Yield : 13.2 g (68 %). ^{1}H NMR (300 MHz, C_6D_6): δ 12.51 (s, 1H, NH), 6.57-6.52 (m, 6H, H_{ar}), 4.87 (s, 1H, *H*C[C(CH_3)NAr]$_2$), 1.70 (s, 6H, HC[C(C*H*$_3$)NAr]$_2$). ^{13}C NMR (75 MHz, C_6D_6): 163.4 (s, HC[*C*(CH_3)NAr]$_2$), 158.5 (dd, $^{F\text{-}C}J$ = 246.70 Hz, 5.06 Hz, C_{ar}), 124.9 (t, $^{F\text{-}C}J$ = 9.63 Hz, C_{ar}), 123.1 (t, $^{F\text{-}C}J$ = 16.77 Hz, C_{ar}), 111.6 (dd, $^{F\text{-}C}J$ = 16.61 Hz, 7.93 Hz, C_{ar}), 98.3 (s, H*C*[C(CH_3)NAr]$_2$), 20.5 (s, HC[C(*C*H$_3$)NAr]$_2$). ^{19}F{^{1}H} NMR (282 MHz, C_6D_6): -121.81. HRMS (EI): m/z : calcd for $[C_{17}H_{14}N_2F_4]^+$: 322.1093; found: 322.1091.

*4.3 Synthesis of the complexes (**2-9**)*

*4.3.1 Synthesis of **2***

To a solution of **1** (2.5 g, 7.76 mmol) in dry ether (20 mL) was added dropwise *n*-BuLi (4.9 mL, 1.6 M solution in hexanes) at -40 ºC. After warming to room temperature and stirring overnight, the yellow solution was concentrated under vacuum until precipitation. After addition of cold pentane, the precipitate was centrifuged and the solution eliminated. The resulting solid was washed with cold pentane, to give rise to **2**, as a yellow crystalline powder. Yield : 2.26 g (72 %). Crystals suitable for X-ray structure analysis were obtained from an ether solution of **2** at -40 ºC. ^{1}H NMR (300 MHz, C_6D_6): δ 6.63-6.38 (m, 6H, H_{ar}), 4.94 (s, 1H, *H*C[C(CH_3)NAr]$_2$), 2.85 (q, ^{3}J = 7.97 Hz, 4H, -OC*H*$_2$CH$_3$), 1.92 (s, 6H, HC[C(C*H*$_3$)NAr]$_2$), 0.84 (t, ^{3}J = 7.97 Hz, 6H, -OCH$_2$C*H*$_3$). ^{13}C NMR (75 MHz, C_6D_6): 167.3 (s, HC[*C*(CH_3)NAr]$_2$), 157.2 (dd, $^{F\text{-}C}J$ = 240.73 Hz, 3.05 Hz, C_{ar}), 131.2 (t, $^{F\text{-}C}J$ = 9.32 Hz, C_{ar}), 121.5 (t, $^{F\text{-}C}J$ = 15.82 Hz, C_{ar}), 111.3 (dd, $^{F\text{-}C}J$ = 17.21 Hz, 8.12 Hz, C_{ar}), 98.4 (s, H*C*[C(CH_3)NAr]$_2$), 66.3 (s, -O*C*H$_2$CH$_3$), 23.34 (s, HC[C(*C*H$_3$)NAr]$_2$), 14.2 (s, -OCH$_2$*C*H$_3$). ^{19}F{^{1}H} NMR (282 MHz, C_6D_6): -124.69.

*4.3.2 Synthesis of **3***

To a solution of **1** (2 g, 6.21 mmol) in dry THF (20 mL) was added dropwise *n*-BuLi (3.9 mL, 1.6 M solution in hexanes) at -40 ºC. After warming to room temperature and stirring overnight, the yellow solution was concentrated under *vacuum* until precipitation. After addition of cold pentane, the precipitate was centrifuged and the solution eliminated. The resulting solid was washed with cold pentane, to give rise to **3**, as an orange crystalline powder. Yield: 1.70 g (68 %). ^{1}H NMR (300 MHz, C_6D_6): δ 6.69-6.40 (m, 6H, H_{ar}), 5.05 (s, 1H, *H*C[C(CH_3)NAr]$_2$), 3.35 (m, 4H, -OCH_2CH$_2$-), 2.01 (s, 6H, s, 6H, HC[C(CH_3)NAr]$_2$), 1.21 (m, 4H, -OCH$_2$CH_2-). ^{13}C NMR (75 MHz, C_6D_6): 166.3 (s, HC[*C*(CH_3)NAr]$_2$), 157.3 (dd, $^{F\text{-}C}J$ = 238.42 Hz, 3.11 Hz, C_{ar}), 132.1 (t, $^{F\text{-}C}J$ = 9.54 Hz, C_{ar}), 120.9 (t, $^{F\text{-}C}J$ = 15.08 Hz, C_{ar}), 111.2 (dd, $^{F\text{-}C}J$ = 18.65 Hz, 8.87 Hz, C_{ar}), 97.0 (s, H*C*[C(CH_3)NAr]$_2$), 67.9 (-O*C*H$_2$CH$_2$-), 25.4 (-OCH$_2$*C*H$_2$-), 23.4 (s, HC[C(*C*H$_3$)NAr]$_2$). ^{19}F{^{1}H} NMR (282 MHz, C_6D_6): -123.75.

*4.3.3 Synthesis of **4***

To a solution of **1** (2.5 g, 7.76 mmol) in dry pentane (20 mL) was added dropwise *n*-BuLi (4.9 mL, 1.6 M solution in hexanes) at -40 ºC. After warming to room temperature and stirring overnight, the resulted precipitate was centrifuged and washed with a small amount of cold pentane, to give rise to **4**, as a yellow crystalline powder. Yield: 1.90 g (74 %). Crystals suitable for X-ray structure analysis were obtained from a hexane solution of **4** at -40 ºC. ^{1}H NMR (300 MHz, C_6D_6): δ 6.45-6.23 (m, 6H, H_{ar}), 4.74 (s, 1H, *H*C[C(CH_3)NAr]$_2$), 1.81 (s, 6H, HC[C(CH_3)NAr]$_2$). ^{13}C NMR (75 MHz, C_6D_6): 168.9 (s, HC[*C*(CH_3)NAr]$_2$), 157.3 (dd, $^{F\text{-}C}J$ = 238.16 Hz, 6.56 Hz, C_{ar}), 130.3 (t, $^{F\text{-}C}J$ = 8.94 Hz, C_{ar}), 121.7 (t, $^{F\text{-}C}J$ = 10.30 Hz, C_{ar}), 111.2 (d, $^{F\text{-}C}J$ = 25.47 Hz, C_{ar}), 100.76 (s, H*C*[C(CH_3)NAr]$_2$), 23.8 (s, HC[C(*C*H$_3$)NAr]$_2$). ^{19}F{^{1}H} NMR (282 MHz, C_6D_6): -126.81.

*4.3.4 Synthesis of **5***

A solution of **2** (200 mg, 0.49 mmol) in diethyl ether (5 mL) was added to a suspension of ZnI_2 (157 mg, 0.49 mmol) in diethyl ether (5 mL) at -40 ºC. After warming to room temperature, the mixture was stirred for 20 h. The resulting pale-yellow clear solution was filtered through Celite to avoid the presence of insoluble residue and concentrated under vacuum until precipitation. After addition of pentane, the resulted precipitate was centrifuged and washed with pentane, to give rise to **5** as a white solid after drying. Yield: 340 mg, 87 %. Crystals suitable for X-ray structure analysis were grown by slow evaporation at room temperature of a saturated solution of **5** in diethyl ether. ^{1}H NMR (300 MHz, C_6D_6): δ 6.68-6.52 (m, 6H, H_{ar}), 4.79 (s, 1H, *H*C[C(CH_3)NAr]$_2$), 3.22 (q, ^3J = 7.07 Hz, 8H, -OCH_2CH$_3$), 1.70 (s, 6H, HC[C(CH_3)NAr]$_2$), 0.89 (t, ^3J = 7.07 Hz, 12H, -OCH$_2$CH_3). ^{13}C NMR (75 MHz, C_6D_6): 169.5 (s, HC[*C*(CH_3)NAr]$_2$), 157.8 (dd, $^{F\text{-}C}J$ = 238.57 Hz, 7.02 Hz, C_{ar}), 127.7 (t, $^{F\text{-}C}J$ = 8.26 Hz, C_{ar}), 124.9 (t, $^{F\text{-}C}J$ = 9.12 Hz, C_{ar}), 111.7 (d, $^{F\text{-}C}J$ = 23.24 Hz, C_{ar}), 96.5 (s,

H*C*[C(CH_3)NAr$]_2$), 65.7 (s, -O*C*H_2CH_3), 23.7 (s, HC[C(*C*H_3)NAr$]_2$), 14.6 (-OCH_2*C*H_3). $^{19}F\{^1H\}$ NMR (282 MHz, C_6D_6): -117.54.

*4.3.5 Synthesis of **6***

A solution of **2** (200 mg, 0.49 mmol) in diethyl ether (5 mL) was added to a suspension of $ZnBr_2$ (110 mg, 0.49 mmol) in diethyl ether (5 mL) at -40 ºC. After warming to room temperature, the mixture was stirred for 24 h. The resulting pale-yellow clear solution was filtered trough Celite to avoid the presence of some residual insoluble material and concentrated under *vacuum* until precipitation. After addition of pentane, the resulted precipitate was centrifuged and washed with pentane, to give rise to **6** as a white solid after drying. Yield: 280 mg, 81 %. Crystals suitable for X-ray structure analysis were grown by slow evaporation at room temperature of a saturated solution of **6** in diethyl ether. *As an insoluble material in adequate aromatic deuterated solvents,* ***6*** *couldn't be characterized by NMR spectroscopy.*

*4.3.6 Synthesis of the mixture of 7**a** and 7**b***

A solution of **2** (200 mg, 0.49 mmol) in diethyl ether (5 mL) was added to a suspension of CdI_2 (179 mg, 0.49 mmol) in diethyl ether (5 mL) at -40 ºC. After warming to room temperature, the mixture was stirred for 24 h. The resulting pale-yellow clear solution was filtered trough Celite to avoid the presence of some residual insoluble material and concentrated under vacuum until precipitation. After addition of pentane, the resulted precipitate was centrifuged and washed with pentane, to give rise to a mixture of **7b** as major product (82 %) and **7a** as minor product (18 %) as a white solid after drying. Total yield: 263 mg, 75 %. Crystals suitable for X-ray structure analysis were grown by slow evaporation at room temperature of a saturated solution in diethyl ether, the measured crystals showing the presence of both complexes in a 1 to 1 ratio. ^1H NMR (300 MHz, C_6D_6) (**7a**): δ 6.59-6.40 (m, 6H, H_{ar}), 4.63 (s, 1H, *H*C[C(CH_3)NAr$]_2$), 3.24 (q, ^3J = 7.05 Hz, 12H, -OC$H_2$$CH_3$), 1.91 (s, 6H, HC[C(C$H_3$)NAr$]_2$), 0.95 (t, ^3J = 7.05 Hz, 18H, -OCH_2CH_3). ^1H NMR (300 MHz, C_6D_6) (**7b**): δ 6.59-6.40 (m, 6H, H_{ar}), 4.68 (s, 1H, *H*C[C(CH_3)NAr$]_2$), 3.24 (q, ^3J = 7.05 Hz, 8H, -OC$H_2$$CH_3$), 1.74 (s, 6H, HC[C(C$H_3$)NAr$]_2$), 0.95 (t, ^3J = 7.05 Hz, 12H, -OCH_2CH_3). ^{13}C NMR (75 MHz, C_6D_6) (mixture of **7a** and **7b**): 173.9 (s, HC[*C*(CH_3)NAr$]_2$), 170.6 (s, HC[*C*(CH_3)NAr$]_2$), 158.4-154.5 (m, C_{ar}), 124.1 (m, C_{ar}), 123.5 (m, C_{ar}), 111.6 (m, C_{ar}), 96.9 (s, H*C*[C(CH_3)NAr$]_2$), 65.8 (s, -O*C*H_2CH_3), 24.5 (s, HC[C(*C*H_3)NAr$]_2$), 23.9 (s,

$HC[C(CH_3)NAr]_2$), 14.8 (s, $-OCH_2CH_3$). $^{19}F\{^1H\}$ NMR (282 MHz, C_6D_6) (**7a**): -119.91 (br). $^{19}F\{^1H\}$ NMR (282 MHz, C_6D_6) (**7b**): -122.12 (s).

*4.3.7 Synthesis of **8***

A solution of **2** (200 mg, 0.49 mmol) in diethyl ether (5 mL) was added to a suspension of HgI_2 (223 mg, 0.49 mmol) in diethyl ether (5 mL) at -40 ºC. After warming to room temperature, the mixture was stirred for 6 h. The resulting yellow clear solution was filtered trough Celite to avoid the presence of some residual insoluble material and concentrated under vacuum until precipitation. After addition of pentane, the resulted precipitate was centrifuged and washed with pentane, to give rise to 8 as a yellow solid after drying. Yield: 324 mg, 77 %. ^1H NMR (300 MHz, C_6D_6): δ 6.56-6.45 (m, 6H, H_{ar}), 4.89 (s, 1H, $HC[C(CH_3)NAr]_2$), 3.00 (q, ^3J = 7.07 Hz, 4H, $-OCH_2CH_3$), 1.97 (s, 6H, $HC[C(CH_3)NAr]_2$), 0.66 (t, ^3J = 7.05 Hz, 6H, $-OCH_2CH_3$). ^{13}C NMR (75 MHz, C_6D_6): 177.1 (s, $HC[C(CH_3)NAr]_2$), 155.3 (m, C_{ar}), 124.5 (m, C_{ar}), 111.4 (m, C_{ar}), 67.1 (s, $HC[C(CH_3)NAr]_2$), 65.5 (s, $-OCH_2CH_3$), 23.3 (s, $HC[C(CH_3)NAr]_2$), 14.0 ($-OCH_2CH_3$). $^{19}F\{^1H\}$ NMR (282 MHz, C_6D_6): -119.6.

*4.3.8 Synthesis of **9***

To a solution of **1** (385 mg, 1.19 mmol) in toluene (10 mL) was added diethyl zinc (1.1 M solution in toluene, 5 mmol, 5.5 mL) at room temperature. The clear solution was heated at 80 ºC for 20 h. After cooling down to room temperature, volatiles were removed under *vacuum*. After dryness, **9** was obtained as a yellow solid with quantitative yield. ^1H NMR (300 MHz, C_6D_6): δ 6.59-6.47 (m, 6H, H_{ar}), 4.95 (s, 1H, $HC[C(CH_3)NAr]_2$), 1.73 (s, 6H, $HC[C(CH_3)NAr]_2$), 1.09 (t, ^3J = 8.12 Hz, 3H, $ZnCH_2CH_3$), 0.38 (q, ^3J = 8.12 Hz, 2H, $ZnCH_2CH_3$). ^{13}C NMR (75 MHz, C_6D_6): 169.5 (s, $HC[C(CH_3)NAr]_2$), 157.0 (dd, $^{F\text{-}C}J$ = 245.56 Hz, 4.66 Hz, C_{ar}), 127.2 (t, $^{F\text{-}C}J$ = 7.26 Hz, C_{ar}), 125.3 (t, $^{F\text{-}C}J$ = 9.55 Hz, C_{ar}), 111.7 (dd, $^{F\text{-}C}J$ = 16.69 Hz, $^{F\text{-}C}J$ = 7.84 Hz, C_{ar}), 98.5 (s, $HC[C(CH_3)NAr]_2$), 22.9 (s, $HC[C(CH_3)NAr]_2$), 11.90 (s, $ZnCH_2CH_3$), -2.9 (s, $ZnCH_2CH_3$).

4.4 X-ray crystallographic studies

Crystals were mounted on a glass fibre and used for a low-temperature (160 K) X-ray structure determination. All measurements were made on a *Nonius KappaCCD* area-detector diffractometer using graphite-monochromated Mo *Kα* radiation (λ = 0.71073 Å) and an

Oxford Cryosystems Cryostream 700 cooler. Data reduction was performed with HKL Denzo and Scalepack[38]. The structures were solved by direct methods using SIR92[39], which revealed the positions of all non-hydrogen atoms. The refinement of the structures was carried out on F^2 by using full-matrix least-squares procedures, which minimised the function $w(F_O^2 - F_C^2)^2$. The weighting scheme was based on counting statistics and included a factor to downweight the intense reflections. Plots² of $w(F_O^2 - F_C^2)^2$ versus F_C/F_C(max) and resolution showed no unusual trends. The *SHELXL97* program was used for all calculations[40]. Crystallographic data are given in Table 1 and 2.

Table 1. Crystallographic data for **1**, **2** and **4**

Compound	**1**	**2**	**4**
Lattice	monoclinic	monoclinic	monoclinic
Formula	$C_{17}H_{14}F_4N_2$	$C_{21}H_{23}F_4LiN_2O$	$C_{33}H_{26}F_8Li_2N_4$
Fw	322.30	402.36	656.47
Space group	$P2_1/n$	$P2_1$	$C2/c$
a/Å	7.1645(1)	7.3289(2)	20.4803(7)
b/Å	9.0770(2)	14.3984(3)	11.1207(3)
c/Å	23.1884(4)	10.0319(2)	14.5422(5)
α/°	90	90	90
β/°	95.111(1)	91.257(1)	109.926(2)
γ/°	90	90	90
V/Å^3	1502.00(5)	1058.36(4)	3113.8(2)
Z	4	2	4
T/K	160(1)	160(1)	160(1)
ρ/g·cm^{-3}	1.425	1.262	1.400
Number of data collected	35464	28140	31562
Number of data used	4375	3195	3575
Parameters refined	215	267	220
R_{int}	0.059	0.061	0.065
R_1 [$I > 2(I)$]	0.051	0.0497	0.0553
wR_2 [all data]	0.1423	0.1205	0.1423
Goodness of fit	1.059	1.093	1.097

Table 2. Crystallographic data for **5**, **6** and the mixture of **7a** and **7b**

Compound	**5**	**6**	**7a** and **7b**
Lattice	monoclinic	triclinic	orthorhombic
Formula	$C_{25}H_{33}F_4I_2LiN_2O_2Zn$	$C_{25}H_{33}Br_2F_4LiN_2O_2Zn$	$C_{54}H_{76}Cd_2F_8I_4Li_2N_4O_5$
Fw	795.67	701.67	1759.50
Space group	$C2/c$	$P\bar{1}$	$Pna2_1$
a/Å	33.6041(5)	15.8743(3)	18.4495(4)
b/Å	17.0227(3)	16.0133(4)	21.5379(5)
c/Å	19.5842(4)	19.1106(3)	16.8342(4)
α/°	90	89.455(1)	90
β/°	124.1846(9)	84.614(1)	90
γ/°	90	70.646(1)	90
V/Å^3	9267.3(3)	4561.9(2)	6689.3(3)
Z	12	6	4
T/K	160(1)	160(1)	160(1)
ρ/g·cm^{-3}	1.711	1.532	1.747
Number of data collected	63466	62067	64658
Number of data used	8162	15931	11701
Parameters refined	607	1019	728
R_{int}	0.057	0.077	0.086
R_1 [$I > 2(I)$]	0.0428	0.0482	0.0377
wR_2 [all data]	0.1229	0.1337	0.0816
Goodness of fit	1.058	1.049	1.026

5. Supplementary data

CCDC 871048-871053 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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